NASA Technical Memorandum 108483

Permeability Testing of Composite Material and Adhesive Bonds for the DC-XA Composite Feedline Program

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TECHNICAL MEMORANDUM

PERMEABILITY TESTING OF COMPOSITE MATERIAL AND ADHESIVE BONDS FOR THE DC-XA COMPOSITE FEEDLINE PROGRAM

I. INTRODUCTION

As part of a technology demonstration program between NASA's Marshall Space Flight Center and McDonnell Douglas Aerospace of Huntington Beach, CA, a composite element is to be constructed that will transport liquid hydrogen on the Delta Clipper (DC-XA) single-stage-to-orbit (SSTO) vehicle. This piece of hardware will be called the LH_2 composite feedline (or more simply just "feedline") throughout the remainder of this report.

The feedline is to demonstrate the following technologies:

- Acceptable hydrogen permeability levels for flight hardware
- Composite-to-composite adhesive joints
- Composite-to-metallic adhesive joints
- Composite-to-composite flange interface
- Composite elbows (90° bends in tubes)
- Composite valve for liquid hydrogen.

The feedline has been designed by McDonnell Douglas with material, adhesive, and all dimensions selected and finalized. The composite material chosen to construct the feedline was IM7/8552 eight harness weave prepreg. A flange at one end of the feedline is also to be made of the same material. A titanium mating piece is to be bonded onto the other end. There are a total of five concentric tubular joints to be bonded with Hysol™ EA 9394 epoxy resin. The bondline thickness is to be 7 to 15 mils for all of the joints. The feedline consists of two major tubular elements, both approximately 2 inches in diameter. One of the tubes contains a 45° elbow, and the other tube contains a 90° elbow. These tubes are to be joined with a splice tube about 2 inches long. This splice tube is to be made of unidirectional IM7/8552 prepreg. A similar splice tube is to join the 90° elbow section with the composite flange.

The lay-up pattern for the woven prepreg material to manufacture the tubular sections is [0/90, ±45, ±45,0/90] which will give a wall thickness of approximately 0.056 in. The pattern for the splice pieces made of the unidirectional tape is $[+60,-60,0]_s$ which gives a wall thickness of approximately 0.030 in.

Since this report only concerns the permeability of the materials in the feedline, the flange lay-up pattern will not be considered.

The overall length of the feedline is about 20 inches. A schematic of the feedline is shown in figure 1.

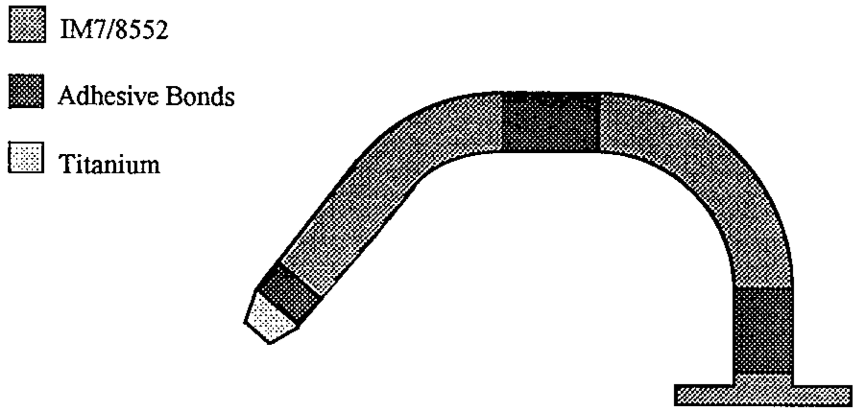

Figure 1. LH_2 composite feedline flight article.

II. PERMEABILITY TESTING

A. Materials

1. IM7/8552 Material. A flat panel consisting of IM7/8552 eight harness weave prepreg was laid up in the configuration of the tubular sections, [0/90, ±45, ±45,0/90]. The panel was hot press cured according to the manufacturer's recommendation. A flat panel consisting of IM7/8552 unidirectional prepreg was laid up in the configuration of the tubular splices, $[+60,-60,0]_s$ and cured in the same manner. After cure test specimens of 1-in diameter disks were machined from the panels using a tungsten carbide coring drill. Some of the discs were cut diagonally across the diameter for microscopy observations. The discs were cleaned with acetone and cotton swabs then placed in individual Ziplock™ bags.

2. Bondline Specimens. In order to assess the permeability of the Hysol™ EA9394 adhesive, the composite discs made from the eight harness weave prepreg were bonded to titanium washers with an outer diameter of 1 in and an inner diameter of 0.5 in. The bondline thickness of the EA 9394 adhesive was controlled by shimming a flat metal plate that would go over the top of the specimens after the adhesive was applied and before it had time to set. The composite discs and the titanium washers were both lightly grit blasted and solvent wiped in the same manner as the feedline bond. Figure 2 shows how these specimens were made.

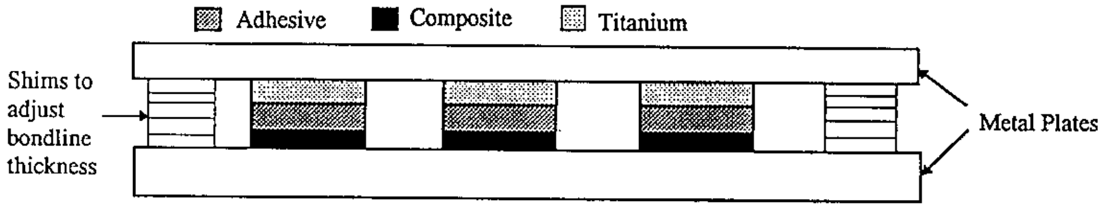

Figure 2. Construction of adhesive permeability samples.

The adhesive was first thoroughly mixed by hand in a plastic beaker and then applied to the titanium washers. The composite discs were then placed on top of the adhesive, and the top metal plate was placed on the shims which had been preset to the correct height to give a 10-mil thick bondline.

For the second batch of these tests, some of the adhesive was mixed and then put under a vacuum to attempt to remove trapped air and some of the adhesive was vacuum mixed with a laboratory scale Ross vacuum mixer.

The resulting bondline permeability test samples were as shown in figure 3.

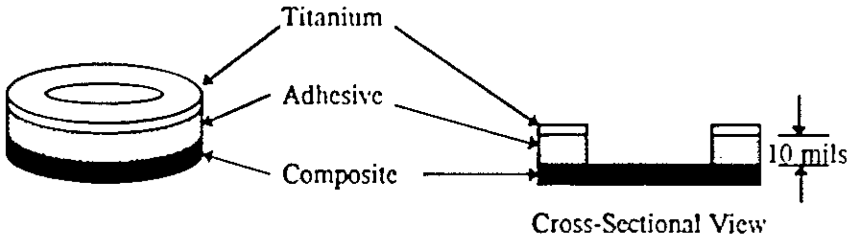

Figure 3. Bondline permeability specimens.

All specimens were cleaned with acetone and a cotton swab then placed in individual ziplock bags.

B. Testing

1. Permeability. A cross section of the permeability apparatus used is shown in figure 4. Basically, the permeant gas (in this study nitrogen) was pressurized against one face of the specimen and a small capillary tube of 0.25-mm diameter with a liquid indicator was placed on the other side of the sample. As gas passed trough the specimen, the escaped gas would go into the capillary tube and lift the indicator as the capillary filled.

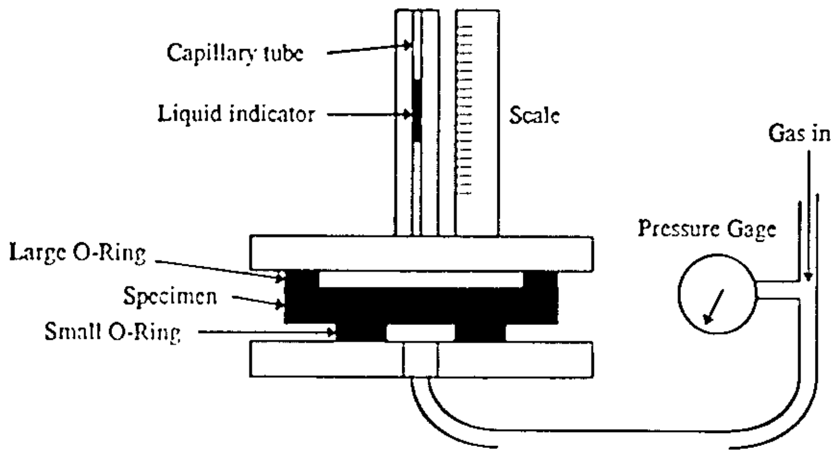

Figure 4. Cross section of permeability apparatus used.

The rate at which the indicator rose could be measured and since the capillary diameter (0.25-mm) was known, the volume of gas that escaped through the specimen per unit time could be determined. The method of determining a permeability value can vary greatly. For this report, the amount of escaped gas per unit time was normalized by the pressure of the permeant gas and by the surface area of composite exposed to the permeant gas for the composite samples and by the inside bondline area of the test samples for the bondline specimens. By "inside bondline area" it is meant the inside perimeter of the titanium washer (0.5 inches by π) times the bondline thickness. This is the area subjected to the pressurized permeant gas. The volume of adhesive can also affect the permeability numbers since leak paths that go through a 1-in length of bondline may not go completely through a 2-in length of bondline. Indeed thicker composite samples do give lower permeability values. However, the surface area exposed to the permeant gas is a much more critical parameter and since most permeability results are reported on a per area basis, area will be used in this report.

Periodically a disc of aluminum was loaded into the permeability test apparatus and tested to assure that the O-rings were properly sealing. The pressure would be turned up to 30 lb/in^2 gauge on one side of the aluminum disc. After approximately 1 h, the liquid indicator was checked to make certain it had not risen by any detectable amount. In addition, all tests samples were loaded at least two different times into the test apparatus. and tested at least five different times for permeability. This was to check for consistency among the results.

All permeability testing was done at ambient temperature.

a. Nitrogen Versus Hydrogen as Permeant. To better understand how the results from the nitrogen permeability testing in this report may relate to the composite feedline hydrogen permeability, an examination of the important molecular constants of the permeation gasses is in order. Table 1 gives the molecular diameter of three gasses as determined by three different methods. Since the permeability is a measure of flow rate, the values as determined from viscosity measurements would be most appropriate.

Table 1. Molecular diameter of three gasses.

Gas	Molecular Diameter, cm		
	From Viscosity	From van der Waal's Equation	From Heat Conductivity
Helium	1.9×10^{-8}	2.6×10^{-8}	2.3×10^{-8}
Hydrogen	2.4×10^{-8}	2.3×10^{-8}	2.3×10^{-8}
Nitrogen	3.1×10^{-8}	3.1×10^{-8}	3.5×10^{-8}

From CRC Handbook of Chemistry and Physics, 54th edition

As can be seen, the helium has the smallest size and would thus be expected to give higher permeation values for the composites (and bonds) tested. The values are not drastically different and it is not expected that the permeability results would vary by an order of magnitude due to the different sizes and viscosities of the gaseous molecules. In this report, the orders of magnitude of permeability is of interest since the variation of values tended to be quite large for a given type of specimen (as will be shown later).

In addition, the feedline test articles were tested with hydrogen gas at pressures up to 70 lb/in^2 and no hydrogen permeation could be detected. This indicates that the measuring apparatus used in this study is more sensitive to permeation than the detection equipment (mass spectrometer "sniffer") used for testing the completed feedline.

While the differences in permeation gases should be noted and kept in mind, for the order of magnitude comparisons made in this study, the type of gas should have little effect on the results.

2. Bondline Thickness. After permeability testing, each bondline specimen had its bondline thickness measured via photomicroscopy. The discs were "flat spotted" at three equally spaced locations around the circumference as shown in figure 5. These areas were then photographed at ×64 and measured from the photograph with a properly calibrated scale to obtain the bondline thickness.

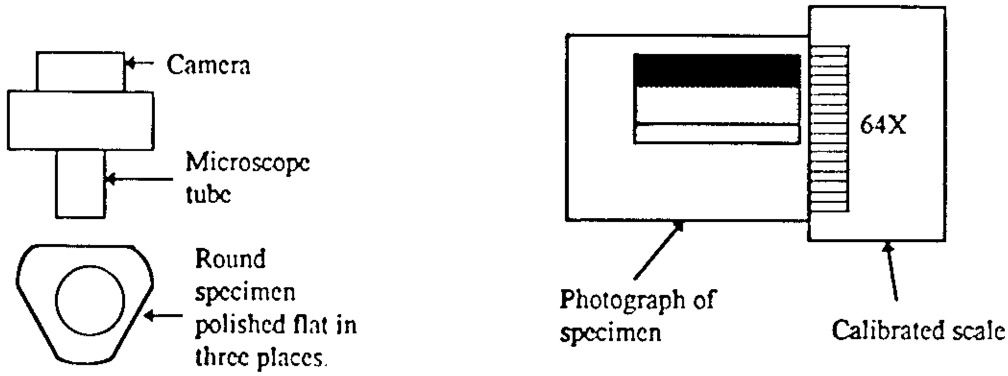

Figure 5. Method of measuring bondline thickness.

From the three measurements on each specimen a good idea of the consistency of the bondline thickness around the perimeter could be obtained. For permeation values, the three thicknesses were averaged.

3. Thermal Cycling. After the specimens (both composite and bondline) were tested for permeability, they were subjected to thermal cycling between 100 °C and LN_2 (–196 °C). This was accomplished by setting the specimens in an air circulating oven set at 100 °C and allowing them to warm for at least 10 min. After they had reached temperature, the specimens were quickly moved straight from the oven into a beaker of liquid nitrogen. The specimens were allowed to soak in the liquid nitrogen for 10 min. The specimens were then placed back into the oven and the entire process repeated for the required number of cycles. When placing the specimens into the oven, they were intentionally dropped onto the oven floor from a height of about 1 ft to induce a small mechanical shock wave through the specimen in an attempt to examine this effect on a sample at cryogenic temperatures.

After the required number of thermal cycles, the specimens were allowed to come to room temperature before further testing.

III. RESULTS

A. Permeability Before Thermal Cycling

1. Composite Permeability Before Thermal Cycling. The permeability of the two types of composite specimens tested before thermal cycling are given in table 2. Note that the specimens had permeability values so low that essentially a measurement could not be made.

Table 2. Permeability results of uncycled composite specimens.

Specimen Number	[0/90, ±45, ±45,0/90].	$[+60, -60, 0]_S$
1	$< 10^{-6}$	$< 10^{-6}$
2	$< 10^{-6}$	$< 10^{-6}$
3	$< 10^{-6}$	$< 10^{-6}$

Values in cubic inch of gas per second per lb/in^2 per square inch of composite surface area.

2. Bondline Permeability Before Thermal Cycling. Only vacuum-mixed adhesive specimens were put through the full test matrix since preliminary results indicated that these specimens tended to be less permeable than the air mixed or the debulked adhesive specimens. In addition, the bond-

lines on the test articles and the flight hardware feedline would contain adhesive that had been vacuum mixed. The preliminary results of the air mixed and debulked adhesive specimens are included in table 3 to show the effects of the type of adhesive preparation. Each value is an average of all the runs performed on that particular bondline sample.

Table 3. Permeability values of bondline specimens before thermal cycling.

Specimen Number	Air Mixed	Debulked	Vacuum Mixed
1	0.0076	0.00018	0.000535
2	0.0034	0.0009	0.00585
3	0.032	—	0.000005

Values in cubic inch of gas per second per lb/in^2 per square inch of adhesive.

Note that the debulked and vacuum mixed samples gave lower permeability values than the air mixed adhesive. The permeability values varied greatly between specimens with the same kind of mix preparation. This indicates the sensitivity to which the permeability results are to the processing of the bondline. Also note that the bondline specimens were much more permeable than the composite specimens.

B. Permeability After Thermal Cycling

1. Composite Permeability After Cycling. After the composite specimens had undergone 4 and 12 thermal cycles between 100 °C and liquid nitrogen (–196 °C), they were again tested for permeability. Table 4 presents the results of the permeability tests after thermal cycling for 4 and 12 cycles.

Table 4. Permeability results of cycled composite specimens.

Specimen Number	[0/90, ±45, ±45,0/90].		[+60, -60, 0]$_s$	
	4 cycles	12 cycles	4 cycles	12 cycles
1	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$
2	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$
3	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$

Values in cubic inch of gas per second per lb/in^2 per square inch of composite surface area.

The values are extremely low (unmeasureable) and do not increase (within sensitivity of the measuring apparatus) as the number of cycles increase.

2. Bondline Permeability After Thermal Cycling. The results from permeability testing on the bondline samples is given in table 5. As mentioned earlier, only the vacuum mixed adhesive specimens were put through the cycling process since this is how the adhesive is to be prepared for the flight hardware.

Table 5. Permeability results after thermal cycling for vacuum-mixed bondline specimens.

Specimen Number	4 cycles	12 cycles
1	0.000535	0.00078
2	0.00585	0.00585
3	0.00005	0.000055

Values in cubic inch of gas per second per lb/in^2 per square inch of adhesive.

No major increase in permeability values was observed in the bondline specimens. It is also worth noting that the specimens remained in the oven at 100 °C for a total of over 72 h. Thus, long-term exposure to low level heat will not degrade the adhesive any appreciable amount. The small mechanical shock waves set up in the specimens by dropping them into the oven while they were at cryogenic temperatures also had no effect on the permeability.

IV. CONCLUSIONS

A. Composite Samples

The composite samples of both types of prepreg material and lay-up configuration demonstrated extremely low (nonmeasurable) permeation values after 4 and 12 thermal cycles between 100 °C and LN_2 (–196 °C). Thus, it is not expected that the composite material in the feedline will be the source of hydrogen leakage as long as the hardware is properly processed.

B. Bondline Specimens

The bondline specimens demonstrated higher permeability values than the composite samples. Despite this, thermal cycling had little effect on the permeation values. In addition, the small shock waves set up in the specimen while at LN_2 temperatures did not cause cracking in the bondline as had been feared. The overall permeation values of the bondline specimens indicate that while some leakage will occur, it will be quite small and well within design limits.

It must be kept in mind that the geometry of the bondline in these samples and in the feedline itself are different. However, since the titanium tube will be outside the composite tube, at low temperatures this bondline will experience a compressive stress which is much more desirable than a tensile stress that tends to pull the bond apart.

APPROVAL

PERMEABILITY TESTING OF COMPOSITE MATERIAL AND ADHESIVE BONDS FOR THE DC-XA COMPOSITE FEEDLINE PROGRAM

By A.T. Nettles

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

Paul H. Schuerer

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Hercules™ IM7/8552 carbon/epoxy and Hysol™ EA 9394 epoxy adhesive bonded between composite/titanium were tested for permeability after various numbers of thermal cycles between 100 °C and liquid nitrogen (–196 °C). The specimens were quenched from the 100 °C temperature into liquid nitrogen to induce thermal shock into the material. Results showed that the carbon/epoxy system was practically impermeable even after 12 thermal cycles. The EA 9394 adhesive bondline was more permeable than the carbon/epoxy, but vacuum mixing tended to minimize the permeability and keep it within allowable limits. Thermal cycling had little effects on the permeability values of the bondline specimens.

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